United States Patent [19]

Ward

[11] **3,899,476**

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[54] **PROCESS FOR MAKING A METHACRYLIC ACID ADDUCT OF LINOLEIC ACID AND PRODUCT**

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[52] **U.S. Cl.**..... **260/97.5;** 260/468 R; 260/514 K

[51] **Int. Cl.**[2]..... **C09F 1/00;** C09F 7/02

[58] **Field of Search**..... 260/97.5, 97.6, 419, 468 R, 260/514 R

[56] **References Cited**

UNITED STATES PATENTS

3,753,968 8/1973 Ward 260/97.5

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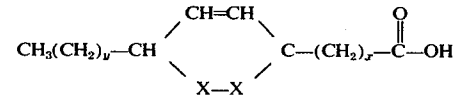
Assistant Examiner—William E. Parker
Attorney, Agent, or Firm—Dennison, Dennison, Townshend & Meserole

[57] **ABSTRACT**

A process for making a Diels-Alder type adduct of methacrylic acid and linoleic acid forming a cycloaliphatic dicarboxylic acid of 22 carbon atoms having the formula



wherein x and y are integers from 3 to 9, x and y together equal 12, and one X is CH_2 and the other X is a $—C(CH_3)COOH$ group.

7 Claims, No Drawings

PROCESS FOR MAKING A METHACRYLIC ACID ADDUCT OF LINOLEIC ACID AND PRODUCT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to the production of a cycloaliphatic dicarboxylic acid of 22 carbon atoms or C_{22}-dicarboxylic acid. More specifically, the cycloaliphatic C_{22}-dicarboxylic acid is prepared by a one-step reaction of methacrylic acid as the dienophile and an iodine catalyst in the formation of a Diels-Alder type adduct with both non-conjugated and conjugated linoleic acid. As used herein, the cycloaliphatic C_{22}-dicarboxylic acid may, in some instances, include minor amounts of dicarboxylic acids of other molecular weight, for example, a C_{21}-dicarboxylic acid.

2. The Prior Art

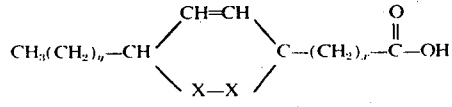
Diels-Alder adduct synthesis, also known as "diene synthesis", involves the reaction of a dienophile with normally conjugated compounds including fatty acids. The Diels-Alder synthesis is well known in the prior art in the reaction of dienophiles with fatty acids as exemplified in a paper entitled "Reactions of Conjugated Fatty Acids. IV. Diels-Alder Adducts of 9,11-Octadecadienoic Acid" by Teter et al., "Journal of Organic Chemistry," Vol. 22, page 512, (1957). In that paper there is described adducts of dienophiles with fatty acids; but there is no disclosure of the reaction of both non-conjugated and conjugated portions of fatty acids in a one-step reaction to form the C_{22}-dicarboxylic acids. Additionally, such other prior art teachings of reactions of fatty acids are described in Ward, U.S. Pat. No. 3,753,968, which describes the production of a C_{21}-cycloaliphatic dicarboxylic acid.

It is, therefore, a general object of this invention to provide a process for making a C_{22}-cycloaliphatic dicarboxylic acid from all of the available linoleic acid in a fatty acid mixture. Another object of this invention is to provide a process whereby tall oil fatty acids, in particular, may be easily separated into a C_{22}-dicarboxylic acid portion and an oleic acid-type portion.

Other objects, features and advantages will be evident from the foregoing disclosure.

SUMMARY OF THE INVENTION

A process for making a Diels-Alder type adduct of methacrylic acid and linoleic acid forming a cycloaliphatic dicarboxylic acid of 22 carbon atoms having the formula



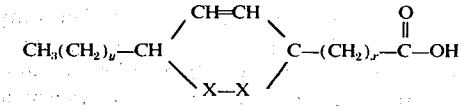
wherein x and y are integers from 3 to 9, x and y together equal 12, and one X is CH_2 and the other X is a $-C(CH_3)COOH$ group, wherein both the non-conjugated and conjugated linoleic acid-portions of the fatty acid are simultaneously reacted with up to 30% by weight of methacrylic acid and 0.01% to 0.50% by weight of said fatty acid mixture of iodine at a temperature between 200°C. and 270°C.

DETAILED DESCRIPTION OF THE INVENTION

The linoleic acid used in the process of the present synthesis may be obtained from any naturally occurring

fatty acid mixture source containing both non-conjugated and conjugated linoleic acids. Especially satisfactory are fatty acid mixtures obtained from tall oil or from such other sources than tall oil as animal or vegetable oils, such as soybean fatty acid, safflower fatty acid, dehydrated castor fatty acids, cottonseed, poppy, as well as pure linoleic acid.

The reaction is carried out in the presence of a minor amount of iodine, the same acting as a catalyst, and thus ensuring complete conversion of both the non-conjugated and conjugated diene linoleic acid and involving an advantageous one-step reaction to a cycloaliphatic C_{22}-dicarboxylic acid having the formula



wherein x and y are integers from 3 to 9, x and y together equal 12, and one X is CH_2 and the other X is a $-C(CH_3)COOH$ group.

Complete conversion to the C_{22}-dicarboxylic acid is further assured by having methacrylic acid present in an amount up to about 30% by weight of the linoleic acid. The catalytic amounts of iodine used is from 0.01% to 0.50% based on the weight of linoleic acid, preferably 0.05% to 0.2% by weight.

As described in U.S. Pat. No. 3,753,968, tall oil fatty acid mixture includes both conjugated and non-conjugated linoleic acid. Methacrylic reacts to convert the total diene portion of said fatty acids to dicarboxylic acid. The amount of methacrylic acid and iodine catalyst used are based upon the total linoleic acid present in the tall oil fatty acid mixture.

The use of large percentages of iodine, i.e., above 0.5% or if the temperature is increased above 270°C. a portion of the linoleic acid is converted to oleic acid and the yield of dicarboxylic acid is thereby decreased. There is a lower limit of feasibility too, for at just slightly milder reaction conditions the rate drops to almost zero. In order to maintain the highest possible yield of dicarboxylic acid from a mixed fatty acid, conditions close to the lower catalyst level and lower temperature are maintained. Selection of the ideal amount of catalyst will depend on the equipment, temperature and time of the reaction. The reaction to produce dicarboxylic acids is carried out at a temperature of 200°C. and 270°C., preferably 230°C. to 260°C. The reaction time at these temperatures and under the preferred catalyst level is about 1 to 2 hours.

The cycloaliphatic C_{22}-dicarboxylic acid of the present invention is useful as a plasticizer, lubricant, soap base, curing agent, or synthetic resin, and chemical intermediate, as in the format on of esters, amides, acid halides, and particularly in the field of synthetic resins involving reaction products of the dicarboxylic acid or functional derivatives thereof, (esters, anhydrides, acid halides, amides), polyesters and polyamides.

The practice of this invention may clearly be seen in the following examples:

EXAMPLE 1

To illustrate the production of a C_{22}-dicarboxylic acid using the process of the subject invention, the following example was performed.

A 1 liter laboratory autoclave was charged with 500 grams of a distilled tall oil fatty acid containing both conjugated and non-conjugated linoleic fatty acids. To the fatty acid mixture was added 0.5 grams of iodine and 77.5 grams of methacrylic acid. The autoclave was sealed and heated at 250°C.–260°C. for 2 hours. Maximum pressure during the reaction was 40 psi. The yield of C_{22} DiAcid as measured by gas/liquid chromatography was 13.9%. The product had a saponification number of 238.5 and an acid number of 215.4. The majority of the remaining portion of the fatty acid mixture following the reaction was an oleic type acid.

EXAMPLE 2

This example illustrates the separation and characterization of the C_{22}-dicarboxylic acid. The fatty acid mixture from Example 1 containing the C_{22}-dicarboxylic acid was pot-distilled under vacuum to remove the mono-carboxylic fatty acids (approximately 55.6% by weight). The undistilled portion was then run through a wiped film evaporator to distill the C_{22}-dicarboxylic acid adduct fraction. The yield of the distilled adduct was 75% based on linoleic acid feed and had the following analysis:

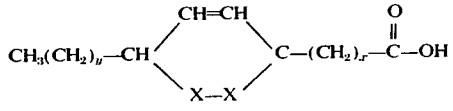
Saponification Number	304
Acid Number	216
Gardner Color Number	5

While the invention has been described and illustrated herein by references to various specific materials, procedures and examples, it is understood that the invention is not restricted to the particular materials, combinations of materials and procedures selected for that purpose. Numerous variations of such details can be employed as will be appreciated by those skilled in the art.

What is claimed is:

1. A process for forming a cycloaliphatic C_{22}-dicarboxylic acid from a fatty acid mixture containing conjugated linoleic acid and non-conjugated linoleic acid comprising,

simultaneously reacting both the non-conjugated and conjugated linoleic acid portion of the fatty acid mixture with up to 30% by weight of said fatty acids, methacrylic acid and 0.01% to 0.50% by weight of said fatty acid mixture of iodine at a temperature between 250°C. and 260°C. to convert the conjugated and non-conjugated linoleic acid portion to a dicarboxylic acid having the formula



wherein x and y are integers from 3 to 9, x and y together equal 12, and one X is CH_2 and the other X is a $—C(CH_3)COOH$ group.

2. The process of claim **1** wherein said fatty acid mixture is a tall oil fatty acid mixture.

3. The process of claim **1** further comprising,

distilling the fatty acid mixture containing the C_{22}-dicarboxylic acid and recovering a linoleic-free fatty acid fraction and a C_{22}-dicarboxylic acid fraction.

4. The product of the process of claim **1.**

5. The product of the process of claim **2.**

6. A cyclohexene C_{22}-dicarboxylic acid Diels-Alder type adduct of methacrylic acid and linoleic conjugated and non-conjucated acids.

7. A cyclohexene C_{22}-dicarboxylic acid Diels-Alder type adduct of methacrylic acid and tall oil fatty acids containing both conjugated and non-conjugated linoleic acid.

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